

Fused Salt Reactions of Organosulfur Compounds

Michael A. Nowak, Bruce R. Utz, Daniel J. Fauth
and Sidney Friedman

U.S. Department of Energy
Pittsburgh Energy Technology Center
P.O. Box 10940
Pittsburgh, PA 15236

INTRODUCTION

The treatment of coal with molten caustic is an effective method for cleaning coal (1). Molten caustic treatment removes not only mineral matter but most of the sulfur, including organic sulfur, from coal. While the chemical processes leading to the removal of inorganic sulfur have been examined (2), the mechanism of organic sulfur removal is less understood. Coal characterization studies suggest that the organosulfur moieties in coal may be largely thiophene-type ring structures (3-5). A preliminary investigation in this laboratory studied the reaction of benzothiophene with sodium and potassium hydroxides (6). Evidence was obtained that o-thiocresolates were intermediates in the desulfurization reaction (Equation 1). The overall reaction is multistep; the ring opening is a key step, since only after conversion to a thiol derivative does desulfurization take place. Our findings on the desulfurization of thiols and thiol derivatives will be discussed here.

EXPERIMENTAL

All reagents were used as purchased from commercially available sources except the thiolate salts, which were prepared as previously described (6). Potassium hydroxide contained approximately 10-12 percent moisture, and all other salts were anhydrous. An "inert fused salt diluent" (IFSD), consisting of a 36:55:9 KCl:LiCl:NaCl mixture by mole percent, was also used and had a eutectic point of 346°C. The hydroxide mixture used was a 60:40 KOH:NaOH mixture by weight (50:50 molar).

Reactions were conducted in commercially available 1/2-inch tubing unions fabricated from corrosion resistant Monel, Inconel, or Carpenter-20 alloys. Before use, the unions were washed with tetrahydrofuran and methylene chloride in order to remove any oils. One end cap was placed on the union and tightened to 30 ft lb. The half-assembled reactor was transferred into a nitrogen-purged glove box, where it was charged with approximately 0.40 gram of the organic compound and, when necessary, 2.40 grams of the powdered hydroxide(s) or salt mixture. The second end cap was placed on the reactor. After removing the reactor from the glove box, the second end cap was tightened to 30 ft lb.

The reactor was bolted in a bracket assembly and immersed in a fluidized sand bath that was preheated to the reaction temperature. For most experiments, mixing was effected by shaking the reactor assembly using a mechanical wrist action shaker. Shaking the reaction vessel had little effect on product distribution. After the specified reaction time, the reactor was cooled rapidly by immersion in tap water. The reactor was opened while submersed in 50 mL methylene chloride to dissolve volatile and neutral organic materials.

Glass reactors were prepared by sealing one end of a six-inch length of heavy-walled Pyrex tubing (12.7-mm-o.d. x 2.4-mm-i.d.). The tube was placed in the glove box and charged with approximately 0.10 gram of organic compound and, where appropriate, 0.40 gram of hydroxide(s) or salt mixture. The tube was

removed from the glove box, freeze-thaw degassed, and sealed under vacuum while the lower portion of the tube remained frozen in liquid nitrogen. After warming to room temperature, the ampoule was loaded into a 3/4-inch stainless steel reactor tee assembly (7) and pressurized to equalize the pressure buildup anticipated within the glass ampoule at reaction temperatures. The tee assembly was then submersed in a preheated fluidized sand bath for the appropriate reaction time, removed from the sand bath, and allowed to cool slowly to room temperature. The pressure was vented from the tee assembly, and the ampoule removed. The ampoule was scored and cracked open while submersed in 50 mL methylene chloride.

The methylene chloride washings were transferred into a flask containing 1,2,4,5-tetramethylbenzene as an internal standard for GLC analysis. If the reactor contained salts, it was then shaken with 50 mL distilled water containing sufficient concentrated HCl to adjust the acidity of the final solution to pH 3. The time required to dissolve the salts completely was generally 10-30 minutes. The aqueous solution was decanted into a separatory funnel, where it was extracted with two 25-mL portions of methylene chloride. The methylene chloride extracts were added to a flask containing an internal standard. Aliquots of the methylene chloride solutions were analyzed by GLC. Products were further characterized by GC/MS. Where necessary, solutions were subjected to pressure filtration through microporous membranes to remove insoluble materials (8). The presence of methylene chloride soluble polymers was determined by careful removal of solvent and volatile materials in vacuo and weighing the residues.

RESULTS AND DISCUSSION

The thermal chemistry of alkyl thiolate salts was first examined at the turn of the century (9), and since then little has been done to reveal the mechanisms of their decompositions. Most studies involved aliphatic thiolates, and only recently has anyone examined alkali metal thiolates (10,11). In general, thiolate salts are known to undergo only one pyrolysis reaction: decomposition at or near their melting point to give an organic sulfide and a metal sulfide (Equation 2).

We chose as our model compounds derivatives of the simplest aromatic thiol, thiophenol. Potassium thiophenolate or sodium thiophenolate were heated at 375°C for thirty minutes in a metal union in the presence of potassium hydroxide, sodium hydroxide, or a mixture of sodium and potassium hydroxides, or the IFSD, or as neat samples. The IFSD is molten at 375°C and was used to simulate the ionic character of the molten hydroxide media while being chemically inert towards organosulfur compounds under these conditions. By comparing the chemistry of thiophenolates in molten caustic, or IFSD, or as neat samples, we hoped to determine whether the caustic reacted with thiolate to produce a sulfur moiety more amenable to desulfurization, thus facilitating bond breaking.

We have found that, in the absence of a catalyst, neat potassium and sodium thiophenolates are stable at 375°C for extended periods of time. When potassium thiophenolate or sodium thiophenolate was treated with a molten 60:40 KOH:NaOH mixture in a corrosion-resistant union (Equation 3), a number of reaction and decomposition products were observed. Some starting material was recovered as thiophenol, and small quantities of phenyl sulfide were obtained. Significant quantities of the desulfurization product, benzene, were observed, but also some biphenyl was obtained. A number of minor products (accounting for less than 28% of the material recovered) were also observed. Methylene chloride insoluble materials that appeared as black solids were sometimes observed. Reactions conducted in the presence of hydrogen led to increased yields of benzene and lower yields of black solids (6). These observations lead us to believe that phenyl radicals are intermediates in these reactions, and that the black solids were being formed by uncontrolled polymerization of some radical species. In some cases, some methylene chloride soluble materials had insufficient volatility to be observed by GLC. These were assumed to be oligomeric materials. Products con-

taining hydroxyl groups (phenol) or several sulfhydryl groups were sometimes observed, but generally these products were insignificant. The yields of desulfurized product from the reaction of sodium thiophenolate in sodium hydroxide or potassium hydroxide (12%-16%) were lower than the yields from the reaction of potassium thiophenolate in sodium or potassium hydroxide (30%-40%).

When reactions were conducted in the same reactors using IFSD as a reaction medium, a significant difference in the chemistry of sodium thiophenolate versus potassium thiophenolate was observed. In the IFSD, diaryl sulfide formation competes with desulfurization. Phenyl sulfide was the only product observed when sodium thiophenolate decomposed in IFSD. Potassium thiophenolate decomposed in IFSD to produce the desulfurized product benzene, although a small amount of phenyl sulfide was also produced.

During the course of these studies, inconsistent results led us to observe carefully the product distributions in the different reactor vessels. Potassium thiophenolate was heated at 375°C for 30 minutes as a neat sample or in IFSD using new, "pristine" reactors. When these reactions were conducted in pristine Inconel or Carpenter-20 reactors, no desulfurization took place (Equation 4). Desulfurization was observed in experiments conducted in pristine Monel reactors. The reactors were then pretreated with molten caustic. Potassium thiophenolate was then reacted in these same reactors, and desulfurization products were observed in all cases (Equation 5). No significant increase in desulfurization was observed in experiments conducted in pretreated Monel reactors. Clearly, the metal walls of these reactors were acting as catalysts in the desulfurization mechanism or as reactants that were causing desulfurization. For Inconel and Carpenter-20 alloys, molten caustic was necessary to "activate" the metal surface.

In order to examine the catalytic effect of the metal species in these reactors, a limited systematic study was undertaken. The alloys from which these reactors were fabricated consists mainly of nickel, with individual alloys containing significant quantities of iron, copper, or chromium along with traces of manganese and other metals. Reactions were conducted in sealed glass ampoules to observe the chemistry of thiophenolates in the absence of any metals. In subsequent reactions, individual metals were added to see if they effect desulfurization. As expected, potassium thiophenolate is unreactive in the absence of any other reagents. Again, in the presence of IFSD, potassium thiophenolate provides phenyl sulfide as the major product. Some starting material was recovered. Reaction of potassium thiophenolate in the presence of caustic did not lead to desulfurization. In the presence of nickel powder or Monel shavings, with or without fused salts, significant quantities of desulfurization products (benzene and biphenyl) are obtained. Potassium thiophenolate in the presence of IFSD and iron powder does not undergo desulfurization.

In an effort to understand further the carbon-sulfur bond breaking processes, the chemistry of thiophenol and diphenyl disulfide was examined. The pyrolysis of aromatic thiols has not been studied as extensively as that of aliphatic thiols. When aromatic thiols or disulfides are heated, the major products are diaryl sulfides (12). There are several papers that report desulfurization products arising from pyrolysis of thiophenol at very high temperatures (700°C) or pyrolysis over catalysts at moderately high temperatures (300°-580°C) (13-15). Flow pyrolysis of diphenyl disulfide of 400°C yields thiophenol and diphenyl sulfide (16).

Our studies show that at 375°C, in the absence of any catalytic species, thiophenol and diphenyldisulfide decompose to phenyl sulfide. When heated in the presence of an active catalyst (Monel shavings, nickel or copper powder), thiophenol or diphenyl disulfide gives phenyl sulfide as its major product, but desulfurization products (benzene and biphenyl) are also observed.

We have observed that naphthalene thiols undergo desulfurization more readily than thiophenol. This is in agreement with observations reported in the literature (15).

CONCLUSIONS

In the presence of fused salts, an increase in the reactivity of thiolate salts is observed perhaps because the fused salts function as solvents, and increase the probability of bimolecular reactions. Bimolecular reaction giving rise to organosulfur species more resistant to desulfurization compete with desulfurization, but in coal, because of the more rigid organic matrix, it is not likely to be a problem.

Caustic is not necessary for desulfurization of thiol derivatives, although it may enhance it. An increase in desulfurization in the presence of caustic may be due to suppression of competing bimolecular reactions or some chemical process that actually speeds the desulfurization reaction. We do not have sufficient evidence to support these or other possible explanations. The desulfurization of aromatic thiols and their derivatives requires a catalyst. One of the species that catalyze these reactions is nickel, but other metals or alloys may also catalyze the desulfurization. In some cases, molten caustic is required to "activate" the catalyst. Additional studies concerning the nature of this catalysis and other possible catalytic species are under way. The chemistries of different aromatic thiols are similar, but changes in the aromatic structure influence their reactivity.

ACKNOWLEDGMENTS

We gratefully acknowledge the technical assistance of Murphy Keller, Thomas Williams, Anthony Selmeczy, and James Knoer. We also acknowledge the Oak Ridge Associated Universities Research Associate Program in which Michael Nowak, Murphy Keller, and Anthony Selmeczy participated.

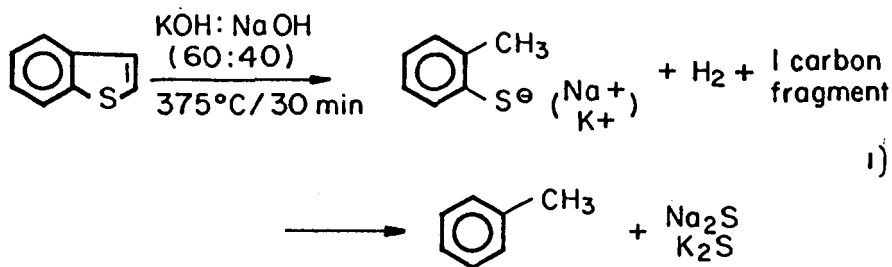
DISCLAIMER

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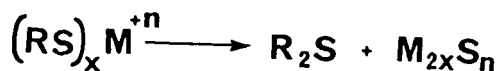
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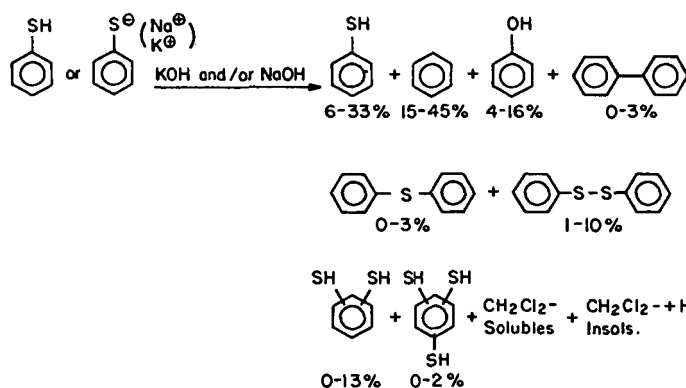
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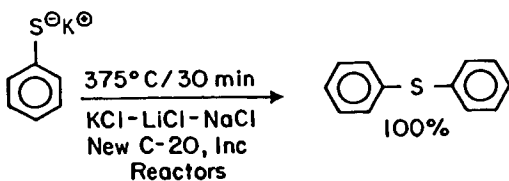
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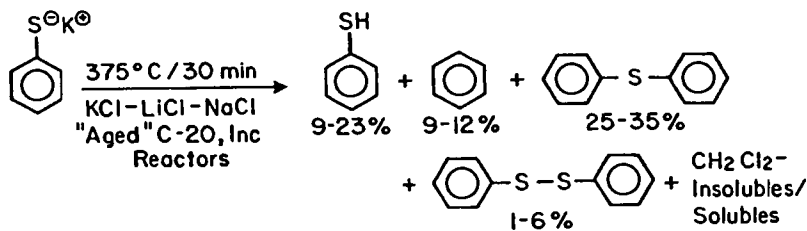
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